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(56) Documents Cited

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(54) Use of polyvinylamine as an adhesion promoter

(57) A process for improving the adhesion of an adhesive material to surface of a negatively charged or polar polymer is provided by treating the polymer surface with a solution of a vinylamine-containing polymer or a salt thereof prior to contacting the polymer surface with the adhesive material.

The negative charge may be produced on polyolefins by treatment such as corona discharge, irradiation or treatment with chemicals such as acids, to produce an anionic surface.

Substrates which may be coated include polypropylene, polyethylene, polyamides, polyvinylidene chloride, polyvinyl chloride, polyethylene terephthalate and cellulose derivatives.

The polyvinylamine may be a homopolymer or a copolymer with polyvinyl alcohol.

The adhesive material is an emulsion of natural rubber, styrene-butadiene, chloroprene, vinyl esters or acrylates.

GB 2 297 503 A

**PROCESS FOR IMPROVING THE
ADHESIVE PROPERTIES OF POLYMER SURFACES**

TECHNICAL FIELD OF THE INVENTION

The present invention relates to methods for improving the adhesive properties of negatively charged or polar polymers.

BACKGROUND OF THE INVENTION

The use of water-based emulsions/suspensions for coating and adhesive applications is a large commodity business. In the area of adhesives, styrene-butadiene, vinyl acetate and acrylate-based emulsions are commonly employed in various applications, including film packaging, carpet backing, pressure-sensitive adhesives, furniture construction, vinyl laminating, general purpose glue/adhesive, and food packaging. Bonding of polymer substrates to woven cloth or non-woven products or other porous products including paper is an important application.

For film lamination, the aqueous vinyl acetate or acrylate emulsions are commonly employed to bond coated or uncoated paper to various films including poly(ethylene terephthalate) (Mylar™), polyethylene, polypropylene, poly(vinylidene chloride) (Saran™), polystyrene, cellulose acetate, aluminum foil, and poly(vinyl chloride). The required properties for film lamination include high solids, film clarity, water resistance, emulsion shear stability, and ability to be sprayed, extruded, or roll coated at high line speeds (e.g., shear rates). Wet tack adhesion (the ability of the adhesive to adhere to a surface prior to evaporation of water) is desired in the case of paper-paper or paper-film lamination. Dry tack adhesion is important where two non-porous surfaces are to be adhered. Of course, the resultant adhesion of the film-paper, film-foil, paper-foil, or film-film laminate is of utmost importance. Extrusion lamination is also a method where adhesion between different substrates is important and improvements are desired. In

this process, the two film surfaces are mated while a layer of molten polymer, such as polyethylene, is simultaneously extruded between the two films. Typically, an adhesion promoting primer is applied to one or both of the film surfaces as a separate operation prior to lamination to improve anchorage to the extruded polyethylene or other hot melt polymeric adhesive layer.

Often the water-based emulsions recited above have limited adhesion to polymer films. One method employed to improve adhesion is by surface treatment of the polymer film, such as by plasma treatment, corona discharge or acid immersion. Another method used to improve adhesion involves adding an adhesion promoter to the adhesive emulsion. U.S. Patents 3,033,707; 3,096,602; 3,140,196; 3,230,135; and 3,361,586 all teach the use of polyalkyleneimine polymers, such as polyethyleneimine, as adhesion promoters in various lamination or heat sealing applications. Additionally, U.S. Patent 5,326,809 teaches a method for preparing poly(vinyl alcohol/vinylamine) copolymers which are useful as protective colloids for vinyl ester and acrylate-based polymer emulsions yielding improved properties as wood adhesives.

SUMMARY OF THE INVENTION

The present invention is a process for improving the adhesion of an adhesive material to the surface of a negatively charged or polar polymer. The polymer surface is coated with a solution comprising from about 0.0001 to 10 wt% of a vinylamine-containing polymer or salt thereof. The coating is carried out such that at least a monomolecular layer of vinylamine-containing polymer or salt thereof adheres to the polymer surface. After the polymer surface is coated with the vinylamine-containing polymer or salt, the adhesive material is applied.

It has been surprisingly found that even monomolecular layers of polyvinylamine or vinylamine copolymers, including polymers of vinylamine salts, applied to the surface of a polar or negatively charged polymer yield adhesion improvements, similar to that

obtained from using much larger amounts of adhesion promoter added directly to the adhesive emulsion. This allows for much less vinylamine-containing polymer to be used to obtain the same desired adhesion properties for which the prior art requires large amounts of adhesion promoter.

5 In addition to improving adhesive properties, the monomolecular layer of vinylamine-containing polymer can be increased in thickness via alternate anionic polymer/poly(vinylamine) dilute solution immersion to build a self-assembly type film. These self-assembled films resist water extraction and yield modified surface properties such as improved printability, antistatic behavior, anti-fogging, friction, antithrombogenic
10 properties and biocompatibility.

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves the treatment of the surface of a polar or negatively charged polymer with a dilute solution of poly(vinylamine), a copolymer of
15 poly(vinylamine) or a polymer comprising a salt of poly(vinylamine) such that at least a monomolecular layer adheres to the surface which resists removal by water. The resultant surface exhibits improved adhesion to typical adhesive materials, such as film laminating emulsion adhesives and hot melt adhesives.

The solution of vinylamine-containing polymer can be applied to any appropriate
20 film or foil surface to improve adhesion properties. The present process is applicable to film-paper, film-cloth, film-foil, paper-foil, foil-cloth, film-film, and foil-foil laminations prepared using wet or dry lamination methods. Suitable films for this process include, but are not limited to polypropylene, polyethylene, cellulosics, polyamides, poly(vinylidene chloride), poly(vinyl chloride), poly(ethylene terephthalate) and the like. Foils include, but
25 are not limited to aluminum and copper. Papers can include, but are not limited to coated and uncoated paper, cardboard, kraft, unbleached and bleached paper. Cloths can include both woven and non-woven (e.g., spun bonded) constructions of either synthetic

or natural fibers. For any of the above substrates which are to be treated with the solution of vinylamine-containing polymer, it is typically necessary that the substrate be either polar or negatively charged. Accordingly, it may be necessary to modify the substrates, or at least their surface, prior to applying the vinylamine solution in order to
5 form anionic groups which can interact with the poly(vinylamine) or vinylamine copolymers.

Any conventional treatment method can be used which is capable of imparting a negative charge on the surface of the film to be coated. For example, polyolefins (such as polyethylene or polypropylene) can be corona discharge treated to yield anionically
10 charged surfaces. Plasma treatment can also be employed for the polyolefins as well as the other polymers of this invention. Acid treatment (e.g., H_2SO_4 , HNO_3 and mixtures thereof) could be employed (via immersion) to yield the desired surface modification. Fluorooxidation would be a particularly effective method of yielding the desired surface modification. Ozone, chlorination, sulfonation, acrylic acid grafting, maleic anhydride
15 grafting, surface oxidation, electron beam exposure, irradiation, UV exposure in the presence of oxygen are additional methods whereby the desired modification could be achieved. Typically, polar polymers do not have to be treated prior to applying the solution of vinylamine-containing polymer.

The solution which is applied to the polymer surface should contain from about
20 0.0001 to 10 wt% of a vinylamine-containing polymer or a salt of a vinylamine-containing polymer, including copolymers thereof. Typically, the vinylamine-containing polymer is in aqueous solution, water/alcohol, or alcohol. The vinylamine-containing polymer can have a wide range of molecular weights, typically ranging from about 5,000 to 1,000,000. In the case of solutions containing copolymers of vinylamine, the copolymers can generally
25 comprise any monomeric units which will copolymerize with vinylamine or a vinylamine salt, or typically the corresponding amide. Examples of monomeric units include vinyl acetate, vinyl alcohol, acrylic acid, maleic anhydride, N-vinylpyrrolidone and other water

soluble monomers. Such copolymers should contain at least 5 mole% vinylamine. Salts of vinylamine-containing polymers can also be used, with examples including polyvinylammonium carbonate and polyvinylammonium chloride.

5 The vinylamine-containing polymers of this invention can be prepared by any conventional synthesis technique known in the art. For example, poly(vinylamine) can be prepared by the synthesis techniques generally set out in U.S. Patent 4,421,602. Additionally, a process for preparing vinylamine/vinyl alcohol copolymers is described in U.S. Patent 5,194,492.

10 The solution of vinylamine-containing polymer can be applied to the surface of the polar or negatively charged polymer in any suitable manner. For example, a dilute solution can be sprayed onto the polymer surface, optionally followed by drying. Alternatively, a roll-coating method could be used or the polymer could simply be immersed into the solution. In any of the techniques, the coated polymer may optionally be rinsed and/or dried prior to applying the adhesive material. The solution applied to the
15 polymer surface should be dilute, i.e., from about 0.0001 wt% to 10 wt% vinylamine-containing polymer based upon the total weight of the solution. Preferred concentrations within this range will depend upon the method of application. The thickness of the applied vinylamine layer can be from one molecular layer thick; i.e., as low as 2nm, to about 50 μ .

20 Additives such as alcohols, surfactants, solvents, defoamers, thickeners, other water soluble polymers and the like can be added to the poly(vinylamine) or vinylamine-containing polymer aqueous solution in order to improve the spreading and wetting of the polymer surface to be modified. This is necessary in some cases as the hydrophobic character of specific polymers may not allow for even distribution of the vinylamine
25 polymer on the surface.

The adhesive material applied to the coated polymer surface is typically an emulsion adhesive or a hot melt adhesive. Examples of suitable emulsion adhesives

include natural rubber, styrene/butadiene, chloroprene, vinyl esters, acrylate emulsions and the like. Polyethylene is a typically used hot melt adhesive. Specific choice of adhesives will depend upon the particular application for which the adhesive is being used, with lamination applications being one of the more common applications.

5 The vinylamine polymer modified surface of the various polymers can be further modified by applying an anionic polymer. The anionic polymer will deposit on the surface a monomolecular layer which will resist water extraction and may impart improved adhesion to specific films. This procedure can be repeated to form layers of poly(vinylamine)/anionic polymer/poly(vinylamine), etc., if so desired to enhance
10 adhesion. A preferred anionic polymer would be poly(acrylic acid).

 Although this invention is primarily concerned with film lamination applications, film or metal surface modification can also be carried out. With negatively charged surfaces, immersion of the surface into a dilute solution containing poly(vinylamine) or a vinylamine copolymer will result in at least one monomolecular layer being deposited.
15 Further rinsing can remove all but one monomolecular layer. This layer can be increased in thickness via alternate anionic polymer/poly(vinylamine) dilute solution immersion. The resultant ultra-thin coating will resist water extraction and will yield modified surface properties. These properties may include (but not be limited to) improved printability, antistatic behavior, anti-fogging, friction, antithrombogenic properties and
20 biocompatibility.

 The following examples are presented to better illustrate the present invention and are not meant to be limiting.

EXAMPLE 1

25 0.1 wt% solutions were prepared by dissolving polymer in deionized water at room temperature. Films of corona treated oriented polypropylene (OPP) and untreated OPP were submerged in the dilute solutions for 1 minute. The films were removed and

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placed in a deionized water bath for 1 minute. The films were removed from the water bath and suspended by binder clips in laboratory conditions (-70°F, 40-55% RH) for 24 hours.

T-peel test specimens were prepared and tested in accord with ASTM method D-413. Airflex 400® (vinyl acetate-ethylene copolymer emulsion (Tg=0°C, 55% solids)) was applied to two inch wide cloth substrates using a number 40 wire-wrapped rod. The non-porous substrate was bonded to the cloth substrate using a seven pound (3.18 kg.) weighted roller. Test specimens were conditioned for 24 hours at 75°F (24°C) and 50% relative humidity. T-peel values were determined on an Instron 1011 at a crosshead speed of 2 in/min (5.08 cm/min). The test results are summarized in Table 1. The control sample was not treated with any dilute polymer solution.

TABLE 1

AIRFLEX 400 CLOTH-TO-SUBSTRATE T-PEEL TEST RESULTS FOR FILMS DIPPED IN DILUTE PVAM OR POLYMIN P AQUEOUS SOLUTIONS

T-PEEL VALUES ARE IN POUNDS PER LINEAR INCH (PLI)

	UNTREATED OPP	CORONA OPP
CONTROL	0.05 ± 0.01	0.69 ± 0.05
	0.05 ± 0.01	0.68 ± 0.05
PVAM	0.05 ± 0.01	1.53 ± 0.09
		1.36 ± 0.13
POLYMIN P	0.06 ± 0.01	0.90 ± 0.06
	0.09 ± 0.02	1.19 ± 0.08

EXAMPLE 2

Solutions of polyvinylamine and Polymin P (polyethyleneimine (PEI) available from BASF) were prepared by diluting each in water/isopropanol (IPA) to achieve 5% active primer and 5% IPA. The IPA was employed as a wetting agent. The primer

solutions were coated on the films set out in Table 2 with a #3 wire rod and allowed to dry at 75°F. One mil low density polyethylene (PE) film corona treated on one side, was employed as a laminating adhesive to simulate extrusion lamination. The PE film was sandwiched between two sheets of the coated films and heat sealed at 300°F, 30 psi for 2 seconds. T-peel adhesion of the coated films to the untreated side of the PE was performed on an Instron at a crosshead speed of 12 in/min the same day. Results in Table 2 show that PVAm provides adhesion equal to or superior to PEI over a broad range of surfaces.

TABLE 2

VALUES IN GRAMS PER LINEAR INCH

	A	B	C	D	E	F
13920-30A**	340*	280	360	1,000*	220*	890*
PVAm	280*	980*	810*	570*	520*	1,070*
PEI	260	870*	130	90	530	430
CONTROL	150	70	16	22	70	60

A MOBIL OPPALYTE 223TE 233TW PP
B MOBIL BICOR AOH (PVOH COATED) PP
C MOBIL 100LCM-W (SLIP MODIFIED) PP
D ALLIED SIGNAL ORIENTED NYLON
E MOBIL 120ABX (ACRYLIC CTD) PP
F POTLATCH 135 LB UNCTD BOARD

* FILM TORE

**13920-30A = PVAm CARBONATE

Most of the films used are commercial grades of polypropylene (PP) used in the flexible packaging industry. The 135 lb. paperboard is similar to that which is extrusion coated with polyethylene to make milk carton stock. In the latter process PEI was used as a primer to anchor the polyethylene to the board. Sample 13920-30A is the carbonate salt of polyvinylamine made by saturating an aqueous solution of the amine with CO₂. The final product contains 39% CO₂ by weight.

In each instance polyvinylamine is found to be equal to or better than PEI (Polymin P) in performance. The carbonate salt is superior to the PEI on all surfaces tested except the Mobil 100LCM-W. The carbonate offers significant economic advantage over PEI or polyvinylamine.

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EXAMPLE 3

A 0.1 wt% solution of PVAm was prepared by dissolving polymer in deionized water at room temperature. Films of corona treated Mylar were submerged in the dilute solution for 1 minute. The films were removed and placed in a deionized water bath for 1
10 minute. The films were removed from the water bath and suspended by binder clips in laboratory conditions (~70°F, 40-55% RH) for 24 hours.

T-peel test specimens were prepared and tested in accord with ASTM method D-413. Airflex 400 was applied to two inch wide cloth substrates using a number 40 wire-wrapped rod. The non-porous substrate was bonded to the cloth substrate using a seven
15 pound (3.18 kg.) weighted roller. Test specimens were conditioned for 24 hours at 75°F (24°C) and 50% relative humidity. T-peel values were determined on an Instron 1011 at a crosshead speed of 2 in/min (5.08 cm/min). The test results summarized below show improved T-peel adhesion for the corona discharged treated Mylar after dipping in dilute PVAm solution in comparison to the control. For comparison, the same procedure was
20 carried out using untreated Mylar. The results are reported in Table 3 below.

TABLE 3

AIRFLEX 400 CLOTH-TO-CORONA DISCHARGED MYLAR T-PEEL TEST
RESULTS FOR FILMS DIPPED IN DILUTE PVAM

25

T-PEEL VALUES ARE IN PLI

	CORONA TREATED MYLAR	UNTREATED MYLAR
CONTROL	0.30 ± 0.04	0.16 ± 0.02
PVAM	1.27 ± 0.18	0.16 ± 0.02

EXAMPLE 4

0.1 wt% solution of PVOH/PVAm copolymers (12 and 20 mole percent VAm) were prepared by dissolving polymer in deionized water at room temperature. Films of corona treated oriented polypropylene (OPP) were submerged in the dilute solutions for 1 minute. The films were removed and placed in a deionized water bath for 1 minute. The films were removed from the water bath and suspended by binder clips in laboratory conditions (~70°F, 40-55% RH) for 24 hours.

T-peel test specimens were prepared and tested in accord with ASTM method D-413. Airflex 400 was applied to two inch wide cloth substrates using a number 40 wire-wrapped rod. The non-porous substrate was bonded to the cloth substrate using a seven pound (3.18 kg.) weighted roller. Test specimens were conditioned for 24 hours at 75°F (24°C) and 50% relative humidity. T-peel values were determined on an Instron 1011 at a crosshead speed of 2 in/min (5.08 cm/min). The test results summarized below show a measurable improvement in T-peel strength for the primed surfaces in comparison to the control sample.

TABLE 4

AIRFLEX 400 CLOTH-TO-CORONA DISCHARGED OPP T-PEEL TEST
RESULTS FOR FILMS DIPPED IN DILUTE PVOH/PVAM COPOLYMER SOLUTIONS

T-PEEL VALUES ARE IN PLI

	CORONA TREATED OPP
CONTROL	0.56 ± 0.07
PVOH/PVAM COPOLYMER (12 MOLE % PVAM)	1.28 ± 0.13
PVOH/PVAM COPOLYMER (20 MOLE % PVAM)	1.41 ± 0.09

EXAMPLE 5

A 0.1 wt% solution of PVAm was prepared by dissolving polymer in deionized water at room temperature. Films of corona treated polyethylene (PE) were submerged in the dilute solution for 1 minute. The films were removed and placed in a deionized water bath for 1 minute. The films were removed from the water bath and suspended by binder clips in laboratory conditions ($\sim 70^{\circ}\text{F}$, 40-55% RH) for 24 hours.

T-peel test specimens were prepared and tested in accord with ASTM method D-413. Airflex 400 was applied to two inch wide cloth substrates using a number 40 wire-wrapped rod. The non-porous substrate was bonded to the cloth substrate using a seven pound (3.18 kg) weighted roller. Test specimens were conditioned for 24 hours at 75°F (24°C) and 50% relative humidity. T-peel values were determined on an Instron 1011 at a crosshead speed of 2 in/min (5.08 cm/min). The test results summarized in Table 5 show improved T-peel adhesion (witnessed as substrate failure) for the corona discharged polyethylene after dipping in dilute PVAm solution in comparison to the control.

TABLE 5

AIRFLEX 400 CLOTH-TO-CORONA DISCHARGED POLYETHYLENE T-PEEL
TEST RESULTS FOR FILMS DIPPED IN DILUTE PVAM

T-PEEL VALUES ARE IN PLI

	CORONA TREATED POLYETHYLENE
CONTROL	1.37 ± 0.13
PVAM	PE SUBSTRATE FAILURE

EXAMPLE 6

Solutions of polyvinylamine and polyethyleneimine were coated and tested as in Example 2 above. The coatings were applied to the untreated side of Melinex 813-48

polyester film from ICI Inc. (This film is supplied with a proprietary coating on one side.)

The heat sealed samples were aged at 40°C and 90% relative humidity for periods of 24 hours and 1 week. Quite unexpectedly, the samples containing PVAm improved in adhesion upon humidity aging while the polyethyleneimine samples lost most of their

5 adhesion. The results are reported in Table 6 below.

TABLE 6

EFFECT OF HUMIDITY ON ADHESION
(GRAMS PER LINEAR INCH)

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	UNAGED	24 HRS 40°C AND 90% RH	7 DAYS 40°C AND 90% RH
PVAm	62	129	159
PEI	51	3	3

Having thus described the present invention, what is now deemed appropriate for Letters Patent is set out in the following appended Claims.

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We claim:

1. A process for improving the adhesion of an adhesive material to the surface of a negatively charged or polar polymer, said process comprising coating said polymer surface with a solution comprising from about 0.0001 to 10 wt% of a vinylamine-containing polymer or a salt thereof, such that at least a monomolecular layer of said vinylamine-containing polymer or salt adheres to the surface of said negatively charged or polar polymer, and subsequently applying said adhesive material to the resultant coated polymer surface.
2. A process in accordance with Claim 1 wherein said vinylamine-containing polymer is polyvinylamine.
3. A process in accordance with Claim 1 wherein said vinylamine-containing polymer is a vinylamine/vinyl alcohol copolymer.
4. A process in accordance with Claim 1 wherein said vinylamine-containing polymer is a copolymer of vinylamine and monomeric units selected from the group consisting of acrylic acid, maleic anhydride, N-vinylpyrrolidone and other water soluble monomers.
5. A process in accordance with Claim 3 wherein said vinylamine/vinyl alcohol contains at least 5 mole% vinylamine.
6. A process in accordance with Claim 4 wherein said copolymer contains at least 5 mole% vinylamine.

7. A process in accordance with Claim 1 wherein said solution contains polyvinylammonium carbonate.
8. A process in accordance with Claim 1 wherein said vinylamine-containing
5 copolymer has a molecular weight from about 5,000 to 1,000,000.
9. A process in accordance with Claim 1 wherein said negatively charged or polar polymer is selected from the group consisting of surface modified polyolefins, surface modified poly(ethylene terephthalate), poly(amides), cloth and
10 paperboard.
10. A process in accordance with Claim 1 wherein said adhesive material is an emulsion adhesive.
11. A process in accordance with Claim 10 wherein said emulsion adhesive is
15 selected from the group consisting of natural rubber, styrene/butadiene, chloroprene, vinyl esters and acrylate emulsions.
12. A process in accordance with Claim 1 wherein said adhesive material is a hot
20 melt adhesive.
13. A process in accordance with Claim 12 wherein said hot melt adhesive is polyethylene.

14. A process in accordance with Claim 1 wherein said vinylamine-containing polymer solution also contains additives selected from the group consisting of wetting agents, surfactants, solvents, defoamers, viscosifiers, other water soluble polymers, and mixtures thereof.

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Claims searched: 1-14

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.O): B2E
Int Cl (Ed.6): B32B; C09D; C09J 139/02
Other: Online: CAS-ONLINE, EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A,P	EP 0644247 A (Air Prod. & Chem. Inc.) Whole document: use of vinylamine polymers as an adhesion promoter in film lamination.	
A	EP 0599245 A (Air Prod. & Chem. Inc.) Whole document: vinylamine/vinyl alcohol co-polymer for use as an adhesion-promoter.	
A	EP 0193959 A (BASF AG) Whole document: use of a polvinylamine layer as an adhesive between two membranes.	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.